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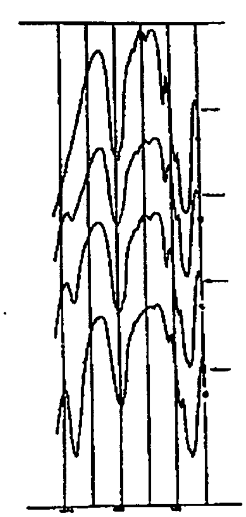
(54) Process for the epoxidation of olefinic compounds.

(57) A process for the epoxidation of olefinic compounds, consisting of reacting said compounds with hydrogen peroxide either introduced as such or produced by substances capable of generating it under the reaction conditions, in the presence of synthetic zeolites containing titanium atoms, of general formula:

$xTiO_2 \cdot (1-x)SiO_2$,

where x lies between 0.0001 and 0.04, and possibly in the presence of one or more solvents, operating at a temperature of between 0° and 150°C, and at a pressure of between 1 and 100 ata.



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This invention relates to a process for the epoxidation of olefinic compounds by means of hydrogen peroxide either introduced as such or produced by substances capable of generating it under the reaction conditions, in the presence of synthetic zeolites containing titanium atoms.

Hydrogen peroxide when in the presence of suitable derivatives of transition metals (Mo, V, W, Ti etc.) is known to be able to attack olefinic double bonds, with the formation of epoxides and/or glycols. The glycol quantity present is a function of the quantity of water introduced with the hydrogen peroxide, and consequently in order to obtain high epoxide selectivity it is necessary to use very concentrated hydrogen peroxide ($\geq 70\%$), with obvious safety problems due to the violent decomposition of the hydrogen peroxide, or to use solvent mixtures able to azeotropically remove the water accompanying the H_2O_2 and the water of reaction.

It is likewise known that polar solvents (of which water is one) kinetically retard the epoxidation reaction.

We have surprisingly found that a synthetic zeolite containing titanium atoms is able to selectively epoxidise the olefins with high epoxide yields even though working with hydrogen peroxide in aqueous solution, and even when diluted to a low concentration such as 10% (the usual being 10-70%).

The subject matter of the present invention is a process for the epoxidation of olefinic compounds consisting of reacting said omp unds with hydrogen per xide either introduced as such or produc d by substances capable of generating it under the reaction conditions, in the presence f synthetic ze lites containing

titanium atoms (titanium silicalites), of th following general formula:

$xTiO_2 . (1-x)SiO_2$,

where x lies between 0.0001 and 0.04, and possibly in the presence of one or more solvents.

The synthetic zeolites used for the epoxidation reaction are described in Belgian patent 886,812, of which we repeat some points illustrating the material and relative method of preparation.

The composition range of the titanium silicalite expressed in terms of molar ratios of the reagents is as follows:

Molar ratio of reagents		preferably
SiO_2/TiO_2	5-200	35-65
OH^-/SiO_2	0.1-1.0	0.3-0.6
H_2O/SiO_2	20-200	60-100
Me/SiO_2	0.0-0.5	0
RN^+/SiO_2	0.1-2.0	0.4-1.0

RN^+ indicates the nitrogenated organic cation deriving from the organic base used for the preparation of the titanium silicalite (TS-1).

Me is an alkaline ion, preferably Na or K.

The final TS-1 has a composition satisfying the formula $xTiO_2 . (1-x)SiO_2$, where x lies between 0.0001 and 0.04, and preferably between 0.01 and 0.025. The TS-1 is of the silicalite type, and all the titanium substitutes the silicon.

The synthetic material has characteristics which are shown up by X-ray and infrared examination.

The X-ray examination is carried out by means of a powder diffractometer provided with an electronic pulse counting system, using the radiation

CuK$\bar{\alpha}$. The titanium silicalites (TS-1) are characterised by X-ray diffraction spectrum as shown in Figure 1b. This spectrum is similar overall to the typical spectrum of silicalite (Figure 1a), however it has certain clearly "single" reflections where double reflections are evident in the pure silicalite spectrum.

Because the spectral differences between TS-1 and silicalite are relatively small, special accuracy is required in the spectral determination. For this reason TS-1 and silicalite were examined by the same apparatus, using Al_2O_3 as the internal standard.

Table 1 shows the most significant spectral data of a TS-1 where $x = 0.017$, and of a pure silicalite.

The constants of the elementary crystalline cell were determined by the minimum square method, on the basis of the interplanar distances of 7-8 single reflections lying within the range of 10-40° 2θ.

A large proportion of the interplanar distances of TS-1 are tendentially greater than the corresponding distances of pure silicalite, although only slightly, which is in accordance with the larger predictable value of the Ti-O bond distance relative to that of the Si-O bond distance.

Passage from a double reflection to a single reflection is interpreted as a change from a monoclinic symmetry (pseudo orthorhombic) (silicalite) to an effective orthorhombic symmetry, "titanium silicalite" (TS-1). In Figure 1, the most apparent aforesaid spectral differences are indicated by arrows.

INFRARED EXAMINATION. TS-1 shows a characteristic absorption band at about 950 cm^{-1} (see Figure 2, spectra B, C and D) which is not

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present in the pure silicalite spectrum (Figure 2, spectrum A), and is als absent in titanium oxides (rutile, anastase) and in alkaline titanates.

Spectrum B is that of TS-1 with 5 mol% of TiO_2, spectrum C is that of TS-1 with 8 mol% of TiO_2, and spectrum D is that of TS-1 with 2.3 mol% of TiO_2.

As can be seen from Figu re 2, the band intensity at approximately 950 cm^{-1} increases with the quantity of titanium which substitutes the silicon in the silicalite structure.

MORPHOLOGY. From a morphological aspect, TS-1 is in the form of parallelepipeds with chamfered edges. A X-ray microprobe examination has shown that the titanium distribution within the crystal is perfectly uniform, thus confirming that the titanium substitutes the silicon in the silicalite structure, and is not present in other forms.

The process for preparing titanium silicalite comprises the preparation of a reaction mixture consisting of sources of silicon oxide, titanium oxide and possibly an alkaline oxide, a nitrogenated organic base and water, the composition in terms of the molar reagent ratios being as heretofore defined.

The silicon oxide source can be a tetraalkylorthosilicate, preferably tetraethylorthosilicate, or simply a silicate in colloidal form, or again a silicate of an alkaline metal, preferably Na or K.

The titanium oxide source is a hydrolysable titanium compound preferably chosen from $TiCl_4$, $TiOCl_2$ and $Ti(alkoxy)_4$, preferably $Ti(OC_2H_5)_4$.

The organic base is tetraalkylammonium hydroxide, and in particular

tetrapropylammonium hydr xide.

The reagent mixture is subjected t hydrothermal treatment in an autoclave at a temperature of between 130 and 200°C under its own developed pressure, for a time of 6-30 days until the crystals of the TS-1 precursor are formed. These are separated from the mother solution, carefully washed with water and dried. When in the anhydrous state they have the following composition:

$xTiO_2.(1-x)SiO_2.\ 0.04(RN^+)_2O.$

The precursor crystals are heated for between 1 and 72 hours in air at 550°C to completely eliminate the nitrogenated organic base. The final TS-1 has the following composition:

$xTiO_2.(1-x)SiO_2$, where x is as heretofore defined.

Chemical and physical examinations are carried out on the products thus obtained.

The epoxidation reaction between olefin and hydrogen peroxide is conducted at a temperature of between 0° and 150°C, at a pressure of between 1 and 100 ata.

Moreover, the epoxidation reaction can be carried out in batch or in a fixed bed, in a monophase or biphase system.

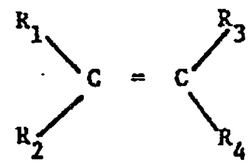
The catalyst is stable under the reaction conditions, and can be totally recovered and reused.

The solvents which can be used include all polar compounds such as alcohols, ketones, ethers, glycols and acids, with a number of carbon atoms which is not too high and is preferably less than or equal to 6.

Methanol or tert.butanol is the most preferred of the alcohols, acetone the most preferred f the ketones, and ac tic or propionic

acid the most preferred of the acids.

The olefinic compounds which can be epoxidated according to the invention are of general formula



where R_1, R_2, R_3 and R_4, which can be the same or different, can be H, or an alkyl, alkylaryl, cycloalkyl or alkylcycloalkyl radical, the alkyl radical having between 1 and 20 carbon atoms, the alkylaryl radical having between 7 and 20 carbon atoms, the cycloalkyl radical having between 6 and 10 carbon atoms, and the alkylcycloalkyl radical having between 7 and 20 carbon atoms.

The radicals R_1, R_2, R_3 and R_4 can constitute saturated or unsaturated rings in pairs.

Finally, the radicals R_1, R_2, R_3 and R_4 can contain halogen atoms, preferably Cl, Br or I, and nitro, sulphonic, carbonyl, hydroxyl, carboxyl and ether groups.

By way of example, the olefins which can be epoxidated by this process are ethylene, propylene, allyl chloride, butene-2, 1-octene, 1-tridecene, mesityl oxide, isoprene, cyclooctene and cyclohexene.

Operating at a pressure exceeding atmospheric pressure is useful if gaseous olefins are used, so as to allow them to be solubilised or liquefied under the reaction conditions. Operating at a temperature exceeding 0°C has an effect on the reaction rate, although this is high even at temperatures close to 0°C.

The manner of operating the process according to the present invention and its advantages will be more apparent from an examination of the

following illustrative examples, which however are not limitative of the invention.

EXAMPLES 1-20

1.5 g of powdered catalyst, 45 cc of solvent and 1 mole of olefin are fed into a 250 cc glass autoclave (olefins which are gaseous at ambient temperature are fed with the autoclave sub-cooled). The autoclave is immersed into a bath temperature-controlled at the required temperature, and 0.3 to 0.6 moles of aqueous H_2O_2 (36% w|v) are fed by a metering pump over a period of 5-10 minutes, under magnetic agitation.

The residual H_2O_2 is checked periodically by withdrawing a solution sample and iodometrically titrating it. When it has practically disappeared, the autoclave is returned to ambient temperature, and the solution analysed by qualitative and quantitative gas chromatography.

The results obtained with various olefinic substrates and the relative reaction conditions are listed in Table 2.

The same epoxidation reactions can also be conducted in a fixed bed, as indicated in the following examples.

EXAMPLES 21-31

3.5 g of catalyst having a particle size distribution of 25-60 mesh are placed in a 6 x 4 mm steel tube 45 cm long and having a volume of 5 cc. A solution containing 200 ml of solvent and 20-40 g of olefin is prepared in a steel autoclave (in the cae of olefins which are gaseous at ambient temperature, the autoclave is pressurised at 15°C with the same olefin until the required weight quantity has been attained). The tube containing the catalyst is immersed in a

temperature-controlled bath, and pumping of the olefin solution is commenced simultaneously with the pumping of the aqueous H_2O_2 solution by means of two metering pumps, the throughputs being regulated so that the molar H_2O_2|olefin feed ratio is between 10 and 90%.

The operating pressure is regulated by means of a suitable valve at the catalytic reactor outlet to a pressure of between 1.5 and 15 ata and in any case greater than the pressure in the autoclave containing the olefin. The effluent is percolated through a condenser at 10°C in order to condense all the condensable products, and is then collected and analysed by gas chromatography.

The results obtained are shown in Table 3.

EXAMPLES 32-34

To demonstrate that the H_2O_2 concentration has no effect on the epoxide-glycol distribution, Table 4 shows by way of example the results obtained with allyl chloride in methanol, under the operating conditions of Examples 1-20.

EXAMPLE 35

40 cc of isopropanol and 10 cc of water are fed into a 250 cc steel autoclave lined with teflon.

The autoclave is immersed in a bath temperature-controlled at 135°C, and pressurised to 35 ata with oxygen, the quantity absorbed being continuously made up.

After an O_2 absorption of 0.2 moles (4.48 normal litres) the mixture is cooled, depressurised and the quantity of H_2O_2 and peroxides in the solution titrated. It contains 0.155 moles of peroxide oxygen (evaluat d a H_2O_2).

40 cc of said solution are transferred to a glass autoclave together with 10 cc of H_2O and 1 gram of titanium silicalite. 5 g of propylene are fed by sub-cooling the autoclave. The autoclave is then immersed under magnetic agitation into a bath temperature-controlled at 20°C. After 35 minutes the solution is analysed by gas chromatography and titrated to obtain the peroxide content. The following results are obtained:

residual peroxides (as H_2O_2)	5.5 mmoles
propylene oxide	110 mmoles
propylene glycol	8,5 mmoles

and thus:

H_2O_2 conversion (peroxides) = 95.56%

propylene oxide selectivity = 92.83%

TABLE 1

TS - 1			Silicalite (a)		
2θ (CuK$\bar{\alpha}$)	Inter-planar distance d(Å)	Rel. Int. (b)	2θ (CuK$\bar{\alpha}$)	Inter-planar distance d(Å)	Rel. Int (b)
7.94	11.14	vs	7.94	11.14	vs
8.85	9.99	s	8.85	9.99	s
9.08	9.74	m	9.08	9.74	m
13.21	6.702	w	13.24	6.687	w
13.92	6.362	mw	13.95	6.348	mw
14.78	5.993	mw	14.78	5.993	mw
15.55	5.698	w	15.55	5.698	w
15.90	5.574	w	15.90	5.574	w
17.65	5.025	w	17.65	5.025	w
17.81	4.980	w	17.83	4.975	w
20.37	4.360	w	20.39	4.355	w
20.85	4.260	mw	20.87	4.256	mw
23.07	3.855	s	23.08	3.853	s
			23.28	3.821	ms
23.29	3.819	s			
			23.37	3.806	ms
			23.71	3.753	ms
23.72	3.751	s			
			23.80	3.739	ms
23.92	3.720	s	23.94	3.717	s

			24.35	3.655	mw
24.41	3.646	m			
			24.60	3.619	mw
			25.84	3.448	w
25.87	3.444	w			
			25.97	3.431	w
26.87	3.318	w*	26.95	3.308	w*
			29.23	3.055	w
29.27	3.051	mw			
			29.45	3.033	w
29.90	2.988	mw	29.90	2.988	mw
30.34	2.946	w	30.25	2.954	w
45.00	2.014	mw*	45.05	2.012	mw*
45.49	1.994	mw*	45.60	1.989	mw*

a) Prepared by the method of U.S. Patent 4,061,724; product calcined at 550°C.

b) vs: very strong; s: strong; ms: medium-strong; m: medium; mw: medium-weak; w: weak; *: multiplet.

TABLE 2

N°	OLEFIN	SOLVENT	t(hours)	T°C	F.R.*	H_2O_2 CONV.	EPOXIDE SELECT.	GLYCOL SELECT.	OTHERS
1	ETHYLENE	CH_3OH	0.5	0°C	50%	99%	85%	5%	10% as glyme
2	"	ACETONE	0.5	25°C	50%	99%	80%	10%	10% as ketal
3	"	t-butyl alc.	0,5	20°C	50%	97%	96%	4%	
4	PROPYLENE	CH_3OH	0.5	0°C	58%	100%	86%	5%	9% as ether
5	"	ACETONE	0.5	40°C	40%	97%	80%	10%	10% as ketal
6	"	t-butyl alc.	0.8	40°C	50%	90%	96%	4%	
7	"	H_2O	1	20°C	50%	98%	72%	28%	
8	ALLYL CHLORIDE	CH_3OH	0.2	70°C	58%	100%	95%	1%	4% as ther
9	"	ACETONE	0.5	70°C	50%	97%	96%	1%	3% as ketal
10	BUTENE-2	CH_3OH	0.5	20°C	40%	100%	85%	5%	10% as ether
11	"	ACETONE	0.8	40°C	50%	98%	82%	10%	8% as ketal
12	"	H_2O	1	25°C	45%	98%	75%	25%	
13	OCTENE 1	CH_3OH	1	65°C	35%	100%	85%	15%	10% as ether
14	"	ACETONE	1	60°C	35%	100%	85%	10%	5% as ketal
15	"	-	2	75°C	30%	100%	83%	17%	
16	1-TRIDECENE	ACETONE	1.5	80°C	30%	95%	92%	8%	

TABLE 2 (contd.)

17	MESITYL OXIDE	ACETONE	1.5	80°C	25%	97%	94%	6%	
18	ISOPRENE	CH_3OH	0.5	90°C	45%	93%	89%	10%	1%
19	CYCLOOCTENE	ACETONE	1.5	80°C	30%	98%	97%	3%	
20	CYCLO HEXENE	ACETONE	1.5	75°C	35%	99%	98%	2%	

$$* \text{F.R.} = \text{feed ratio} = \frac{\text{moles } H_2O_2 \text{ fed}}{\text{moles olefins fed}}$$

TABLE : 3

N°	OLEFIN.	SOLVENT.	T°C	P.K.	PRODUCTIV. Kg/h x 1	H_2O_2 CONVERS.	EPOXIDE SELECT.	GLYCOL SELECT.	OTHERS %	
21	ETHYLENE	CH_3OH	10	45 %	3.02	99%	88 %	3%	9%	as glycol monomethylether
22	"	ACETONE	10	50 %	2,00	92%	91%	5%	4%	as glycol ketal
23	PROPYLENE	CH_3OH	15	68 %	4,15	98%	88.5%	1.5%	10%	as glycol monomethyl ther
24	"	ACETONE	15	55 %	1.55	90%	92%	6%	2%	as glyc l ketal
25	"	t-butyl alc.	20	55 %	2.20	85%	96%	4%	-	
26	ALLYL Chloride	CH_3OH	70	60 %	8.52	100%	98%	1%	1%	as glycol mono. eth r
27	"	ACETONE	70	60 %	4.53	92%	98%	2%	-	
28	BUTENE-2	CH_3OH	40	45 %	5,35	98%	77%	20%	3%	as glycol monoether
29	"	ACETONE	40	50 %	3,70	92%	75%	15%	10%	as ketal
30	OCTENE-1	ACETONE	80	35 %	2.35	99%	80%	15%	5%	as ketal
31	CYCLOHEXENE	CH_3OH	80	40 %	2.12	99%	83%	7%	10%	as glycol monomethylether

TABLE 4

N°	SOLVENT	H_2O_2 CONC. % w/v	F.R.	t(hours)	T°C	EPOXIDE SEL.	GLYCOL SEL.	OTHERS
32	CH_3OH	10%	40%	0.5	15°C	85.2%	5.5%	9.3%
33	" "	36%	40%	0.5	15°C	86.0%	6.2%	7.8%
34	" "	60%	40%	0.5	15°C	84.7%	4.8%	10.5%

CLAIMS:

1. A process for the epoxidation of olefinic compounds, characterised by reacting said compounds with hydrogen peroxide either introduced as such or produced by substances capable of generating it under the reaction conditions, in the presence of synthetic zeolites containing titanium atoms, of the following general formula:

$xTiO_2.(1-x)SiO_2$

where x lies between 0.0001 and 0.04, and possibly in the presence of one or more solvents.

2. A process as claimed in claim 1, characterised in that the epoxidation reaction is conducted at a temperature of between 0° and 150°C, and at a pressure of between 1 and 100 ata.

3. A process as claimed in claim 1, wherein the hydrogen peroxide is in dilute aqueous solution.

4. A process as claimed in claim 1, wherein the hydrogen peroxide in the aqueous solution is between 10 and 70% w/v.

5. A process as claimed in claim 1, wherein the solvent is polar.

6. A process as claimed in claim 5, wherein the polar solvent is chosen from alcohols, glycols, ketones, ethers and acids, having a number of carbon atoms less than or equal to 6.

7. A process as claimed in claim 6, wherein the alcohol is methanol or tert.butanol.

8. A process as claimed in claim 6, wherein the ketone is acetone.

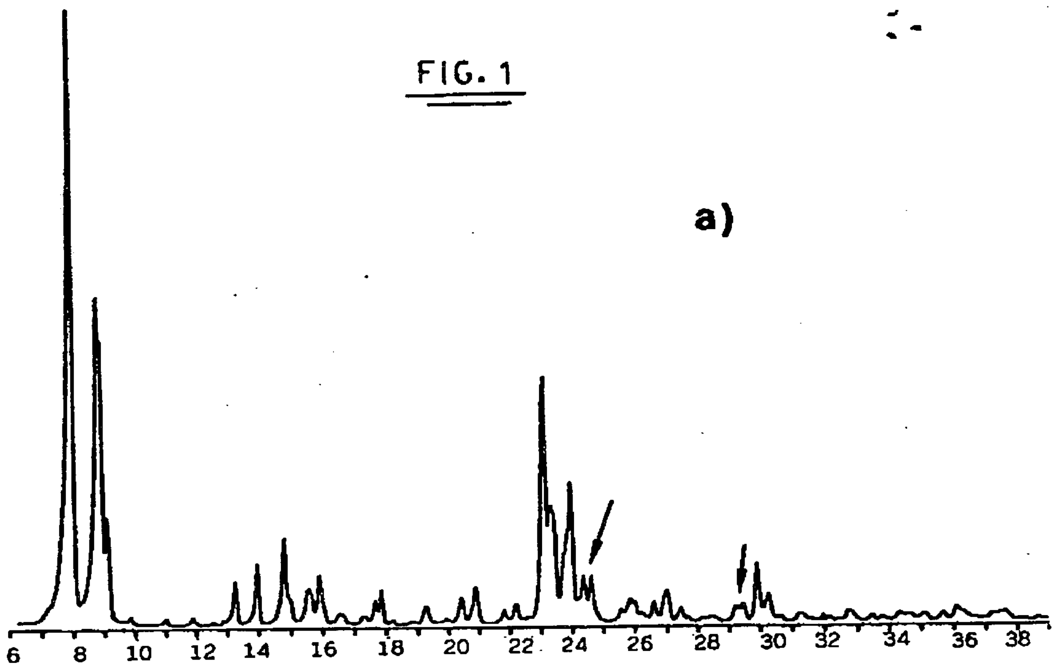
9. A process as claimed in claim 6, wherein the acid is acetic

acid or propionic acid.

10. A process as claimed in claim 1, wherein the olefinic compound is chosen from ethylene, propylene, allyl chloride, butene-2, 1-octene, 1-tridecene, mesityl oxide, isoprene, cyclooctene and cyclohexene.

FIG. 1

a)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b)

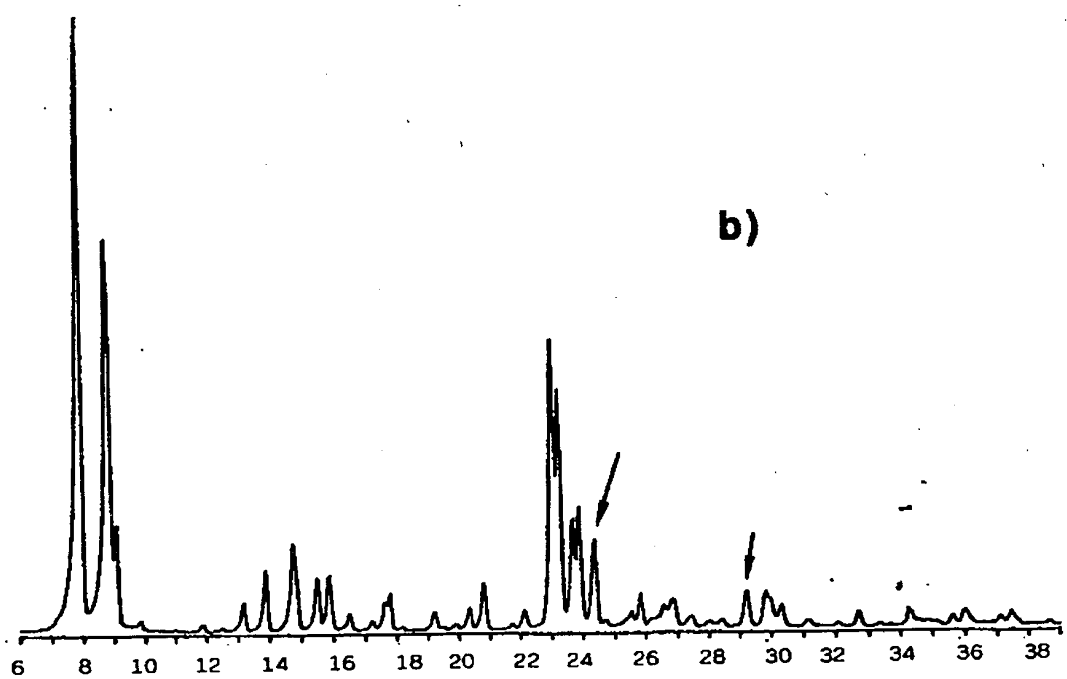
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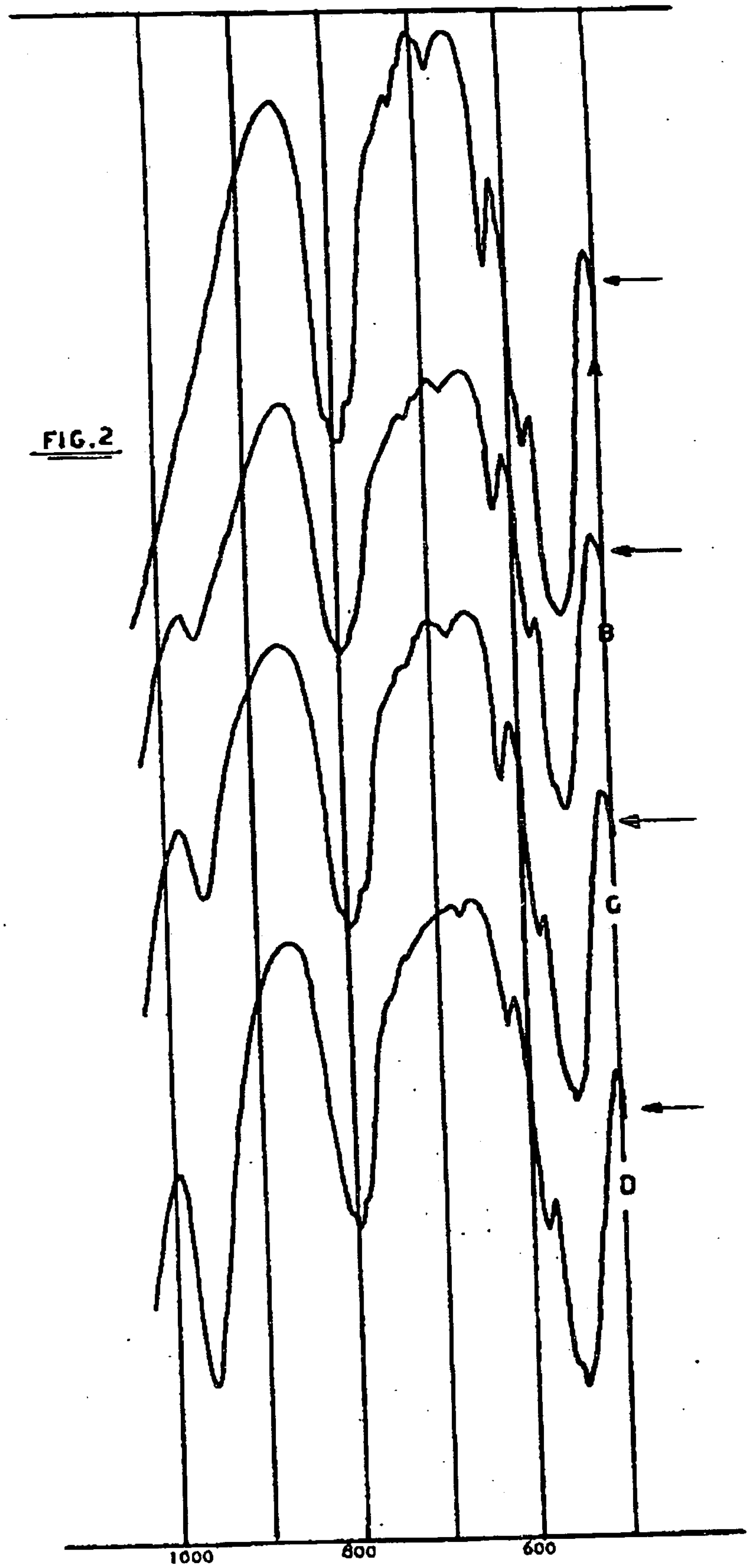
FIG.2



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Application number

European Patent Office

EUROPEAN SEARCH REPORT

EP 83 20 1040

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
Y	GB-A-1 583 398 (PRODUITS CHIMIQUES UGINE KUHLMANN) * Whole document *	1-10	C 07 D 301/12 C 07 D 303/04

Y	GB-A-2 083 816 (ANIC SpA) * Whole document *	1-10	

Y	US-A-2 870 171 (C.M. GABLE) * Whole document *	1-10	

			TECHNICAL FIELDS SEARCHED (Int. Cl. 3)
			C 07 D 301/00 C 07 D 303/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	28-10-1983	ALLARD M.S.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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